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Synthesis and electrochemical study of 4,4′,5-tris(methylthio)-5′-{2-[4,6-di(thiophen-2-yl)-1,3,5-triazin-2-yloxy]ethylthio}tetrathiafulvalene

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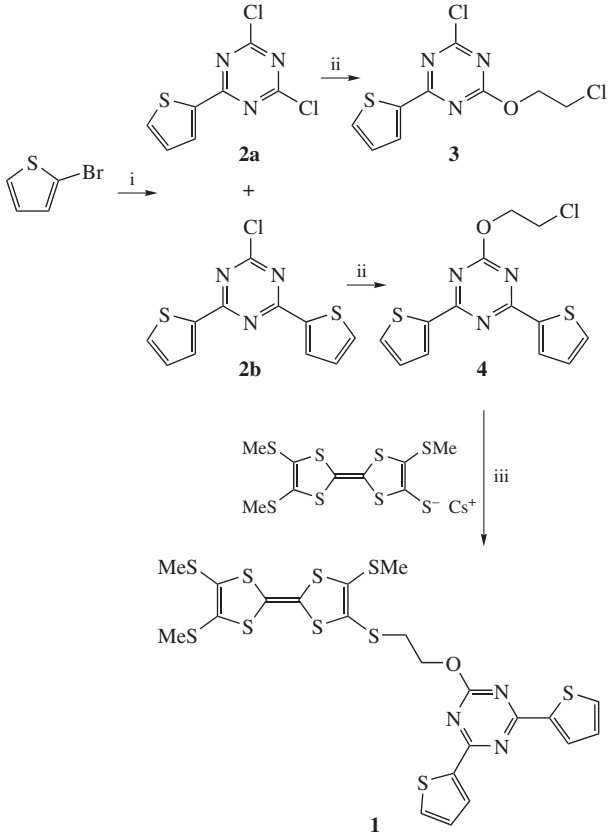
New unsymmetrical 4,4′,5-tris(methylthio)-5′-{2-[4,6-di(thiophen-2-yl)-1,3,5-triazin-2-yloxy]ethylthio}tetrathiafulvalene bearing a polymerizable moiety has been designed and successfully synthesized; its electrochemical properties, susceptibility towards polymerization and crystal structure have been determined.

In recent years considerable efforts have been directed towards the synthesis of conjugated monomers, oligomers and polymers which could be used for creation of various electronic devices of organic electronics.[1] The electron transport in them might be essentially improved by introducing into a conjugation chain any electron-withdrawing fragments of high electron affinity. If these fragments are disposed between π-enriched heterocycles, the corresponding polymers can possess p- and n-type conductivity.[2–4] Along with the synthesis and investigation of conjugated polymers, those of π-donors capable of forming ion-radical salts (IRS) and charge-transfer complexes (CTC) are of stable interest. Sulfur-containing heterocycles such as substituted tetrathiafulvalens (TTFs) belong to this promising family of compounds. The modern trend in the field of organic electronics is to merge in the structure of one molecule the powerful electron-enriched and powerful electron-deficient fragments in order to achieve an electrochemical amphotericity of the final compound.[5] On the other hand, it seems interesting and promising to combine within one molecule the polymerizable moieties and TTF units.[6–12]

The current work presents the synthesis and electrochemical study of a new TTF equipped with electron-deficient 1,3,5-triazine cycle bearing two electron-rich thiophene fragments, compound **1**.†

Replacement of one of the chlorine atoms in compounds **2a** and **2b** by 2-chloroethoxy group affords products **3** and **4**, respectively. This substitution was found to proceed smoothly in 2,4-dichlorotriazine **2a** and to give triazine **3** (85% yield), whose molecular structure was confirmed by X-ray analysis.‡ The similar



Scheme 1 *Reagents and conditions*: i, Mg, THF, then cyanuric chloride, THF, reflux, 10 h; ii, 2-chloroethanol, acetone, K_2CO_3, reflux, 24 h, TLC monitoring; iii, DMF, Ar, 40–45 °C, 6 h.

† For the experimental details of reactions depicted in Scheme 1 and characteristics of compounds **1**–**4**, see Online Supplementary Materials.

‡ *Crystal data for* **1**. Red prism 0.20×0.07×0.03 mm, $C_{22}H_{19}N_3OS_{10}$, M = 662.00, orthorhombic, space group $Pna2_1$, a = 18.1856(7), b = 5.3309(2) and c = 29.3537(13) Å, V = 2845.7(2) Å^3, Z = 4, d_{calc} = 1.545 g cm^{-3}, μ = = 0.798 mm^{-1}. The X-Ray diffraction data for compound **1** were collected on an Xcalibur S automatic single-crystal diffractometer (graphite-monochromated MoKα radiation, ω-scan) at 295(2) K. 13638 reflections were collected in the range 2.64 < θ < 28.32°, 6097 independent reflections (R_{int} = 0.0356), 3228 reflections with $I > 2\sigma(I)$, completeness to θ = 28.32°, 98.0% The structure was solved by direct methods and refined by the full-matrix least-squares method using SHELX-97.[12] The H atoms were positioned geometrically using the riding model. Final R indexes: R_1 = = 0.0377, wR_2 = 0.0577 [$I > 2\sigma(I)$], R_1 = 0.0904, wR_2 = 0.0622 (all data), S = 1.005. Absolute structure parameter 0.05(6). The largest difference peak and hole 0.270 and –0.213 e Å^{-3}.

Crystal data for **3**: light-yellow crystals, $C_9H_7Cl_2N_3OS$, M = 276.14, monoclinic, space group $P2_1/n$, a = 9.8940(11), b = 9.7768(7) and c = = 12.4049(11) Å, β = 101.912(9)°, V = 1174.11 Å^3, Z = 4. The X-Ray diffraction data for compound **3** were collected on an Xcalibur S automatic single-crystal diffractometer (graphite-monochromated MoKα radiation, ω-scan) at 295(2) K; 2894 independent reflections, 1605 with $I > 2\sigma(I)$. Final R_1 = 0.0448 [$I > 2\sigma(I)$].

CCDC 876567 and 876568 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

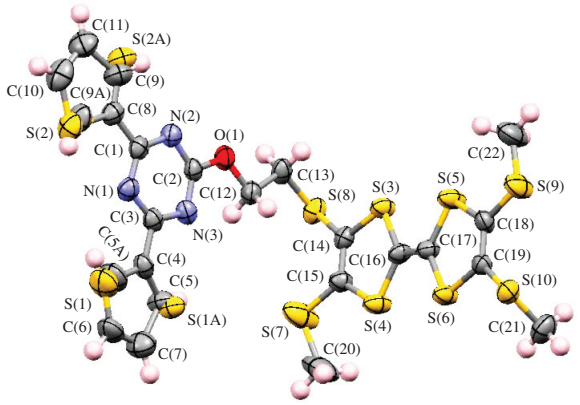


Figure 1 Molecular structure of TTF **1** with atom-labeling scheme.

substitution in compound **2b** proceeds more difficult and provides the 41% yield of the product **4**. The subsequent nucleophilic substitution of its chlorine atom under the action of cesium 4′,5,5′-trimethylthiotetrathiafulvalene-4-thiolate[13] resulted in the target compound **1**.[12,13] This compound gives well-formed crystals of deep ruby colour which can be explained by the presence of two highly conjugated fragments of opposite electronic character, linked with each other by a four-membered bridge. Figure 1 shows a general view of molecular structure of **1**, solved with X-ray crystallography.‡ The morphology of the crystal and crystal packing are presented in Figures 2 and 3, respectively.

Bond lengths and angles of compound **1** are not deviated from the values standard for this class of compounds. The OCH_2CH_2 moiety has antiperiplanar conformation. 2-Thienyl moieties are disordered in two positions with coefficients of occupancy 0.5/0.5 and 0.6/0.4. The angle between triazine and TTF moieties least-squared planes is 88.7°, the deviation of the atoms in the triazine ring from the plane is <0.006 Å, the deviation of the first thienyl substituent atoms is <0.1 Å. For the second thiophene ring the deviation of its atoms from the triazine ring plane increased up to 0.36 Å. Deviation of the atoms of the TTF moiety from least-squared plane is less than 0.1 Å. Noncentrosymmetric crystal packing is formed by piles of molecules oriented along *b* axis. No significant intermolecular short contacts are observed in the molecule packing.

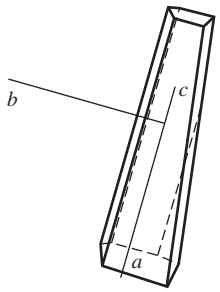


Figure 2 Morphology of TTF **1** crystal.

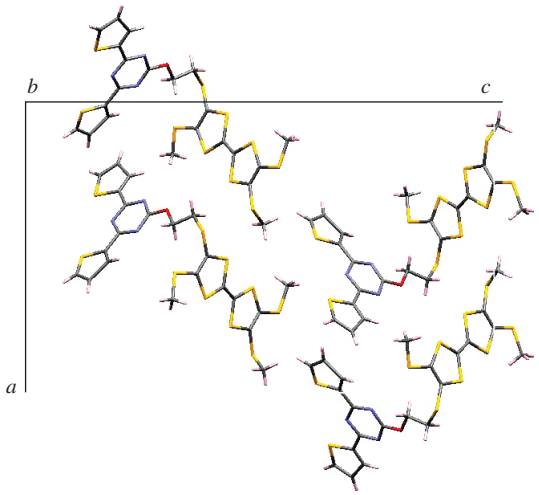


Figure 3 Crystal packing of TTF **1** (view along the *b* axis).

Table 1 Electrochemical characteristics of TTF **1** and its analogues.

TTF	E_a^1/mV	E_a^2/mV	E_a^3/mV	E_c^1/mV	E_c^2/mV
1	636	1003	2024	463	834
5	688	1043	—	550	897
6	618	970	—	477	826

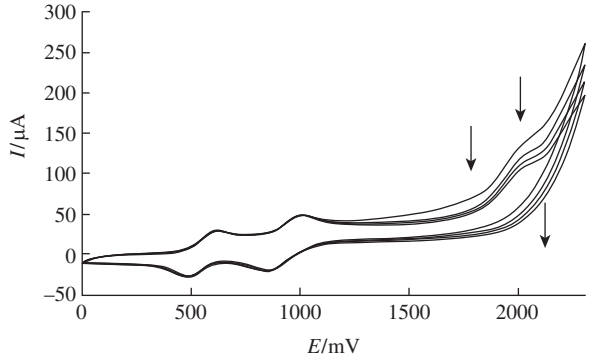
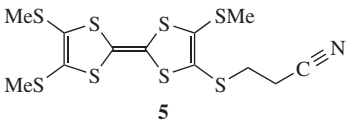


Figure 4 Cyclic voltammogram of TTF **1** (V_{scan} = 100 mV s^{-1}, $[Et_4NPF_6]$ = = 0.1 mol dm^{-3}, [**1**] = 1 mmol dm^{-3}).

The presence of two thiophene moieties with unsubstituted α-C atoms in the molecule of TTF **1** supposes the possibility of its chemical and electrochemical polymerization. The electrochemical behaviour of this TTF was studied by cyclic voltammetry.§ Compound **1** exhibits three oxidation peaks (E_a) and two reduction peaks (E_c) (Table 1, Figure 4). The first two intense reversible oxidation peaks refer to the TTF core oxidation processes – the radical cation (E_a^1) and dication (E_a^2) formation, that is an inherent feature of the electrochemical oxidation of all compounds including TTF core and can serve as additional confirmation of its structure. The third peak (E_a^3) formation is most likely caused by the thiophene fragments oxidation. The electrochemical oxidation of **1** performed on a transparent ITO electrode surface resulted in formation of a light-yellow film insoluble in acetonitrile, acetone, DCM.

For comparison, we have studied electrochemical properties of two related previously synthesized TTFs **5**[14] and **6**[15] (see Table 1). For this purpose we used the same conditions and the same equipment as in the case of the target compound **1**. The presence of an electron-deficient triazine moiety in molecule of **1** led to



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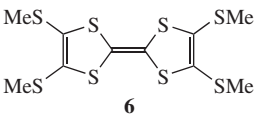

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§ Cyclic voltammograms of **1** were recorded at ambient temperature with potentiostat P8 (voltammetric stand EM-04) using a standard three-electrode cell with a glassy-carbon or transparent ITO (indium-tin oxide) coated glass plate working electrode, a platinum auxiliary electrode and an Ag/AgCl reference electrode. The supporting electrolyte $Bu_4N^+PF_6^-$ (0.1 mol dm^{-3}), monomer concentration, 1 mmol dm^{-3}, the scan rate (V_{scan}) 50–100 mV s^{-1}.

increase in E_a^1 (E_a^2) and E_c^1 (E_c^2) values if compared with those of **6**, including four tetramethylthio groups. At the same time, they do not exceed potential values of **5**, bearing electron-withdrawing group such as $SCH_2CH_2C{\equiv}N$.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.05.011.

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